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Rotational analysis of the $^2\Sigma$-$^2\Sigma$ system of AlO

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With 2 figures in the text

ABSTRACT

A rotational analysis of the well-known $^2\Sigma$-$^2\Sigma$ system has been carried out, in which the levels $v'=0$, 1, 2 and 3 and $v''=$ 0, 1, 2, 3, 4 and 5 have been studied. No perturbations or predissociations have been found in the region analysed. Rotational and vibrational constants have been derived.

Introduction

An intense band-system ascribed to the AlO molecule has been known for many years. Pomeroy (1927) showed that the transition is $^2\Sigma$-$^2\Sigma$ and analysed some of the bands. In 1937 Sen performed rotational analyses of further bands. Dehalu extended the analysis of the 0–0 band to high rotational quantum numbers (1937). She reported an intensity anomaly in the P-branch at $K=129$, and interpreted this as a predissociation in the upper level, corresponding to a dissociation energy of 3.8 eV for AlO. Later Rosen (1944, 1945, 1946) considered that the intensity anomaly arose from a predissociation in the lower state. He considered that this view was confirmed by intensity variations in other parts of the spectrum. Thus he concluded that the predissociation starts at $K=60$ in $v''=6$, at $K=44$ in $v''=7$ and at $K=18$ in $v''=8$; bands with $v''\geq 9$ were said to be absent. These conclusions were made without rotational analysis. Rosen's interpretation would mean that the dissociation energy of AlO ought to be 0.9 eV. Roy (1939) made measurements of the AlO system and gave a vibrational equation for the heads. He found bands with v'' as high as 11.

Experimental

An aluminium arc was used as a source of light. ($\sim$5 A, 220 V.D.C.)

Some of the bands have been photographed in a Bausch and Lomb plane grating (resolwing power $\sim$300000). Going to shorter wavelengths the inverse dispersion for the 0–0 band alters from 0.37 to 0.43 Å/mm. The whole spectrum was also taken with a Wood concave grating (inverse dispersion 1.2 Å/mm, resolving power $\sim$100000). Iron lines were used for comparison.

Structure of the bands

The following bands have been analysed: 0–0, 0–1, 0–2, 1–1, 1–2, 1–3, 2–4 and 3–5. The 0–0 and 1–1 bands were measured from the plane grating exposure, the

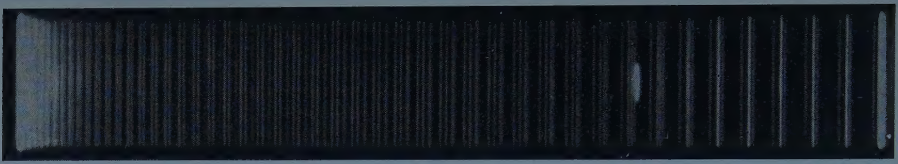

Fig. 1.

others from the concave grating exposures. Special efforts have been made on the 0–0 band and the 0–2 sequence bands. Thus in 0–0 P-lines from $K=4$ up to $K=144$ and R lines from $K=21$ to $K=144$ have been found. The intensity anomaly effect by Dehalu was shown to be the result of the use of a spectroscopic instrument of too low resolving power. A microphotometer trace shows that the intensity varies according to a normal Boltzmann distribution. A reproduction of this has already been published (Lagerqvist, Nilsson & Barrow, 1956). Dehalu also reported several small perturbations in the 0–0 band. We have not been able to find any of these. Fig. 1 gives a reproduction of the 0–0 band taken in the plane grating (magnification $\sim 2\times$).

Originally we had intended to analyse bands with $v''=6$ and 7. To get information about the rotational structure in these levels one ought to investigate sequences such as $\Delta v = -2$ and -3. The sequence $\Delta v = -3$ is, however, very weak, so that we have only examined the bands with $\Delta v = -2$. The 4–6 band is the fifth band of this sequence and is very badly overlapped by the branches from the preceding bands. We have therefore not analysed this band: to get an unequivocal analysis of this band it would be necessary to make new exposures with the plane grating.

As the wave-numbers for several of the bands analysed here have already been given (Pomeroy, Sen), the new measurements will not be given in detail. The following P- and R-lines have been analysed.

Band	P-lines	R-lines	Band	P-lines	R-lines
0–0	4–144	21–144	1–2	14–67	26–67
0–1	23– 80	23– 75	1–3	15–71	18–77
0–2	11– 68	30– 77	2–4	31–73	33–70
1–1	2–100	35–100	3–5	34–70	35–70

In $^2\Sigma$-$^2\Sigma$ bands we have two P and two R branches, representing transitions between F_1 and F_2 rotational levels. We know from intensity relations (Mulliken, 1931) that an F_1 line is a little more intense than the F_2 line. This difference increases with decreasing K-number. Microphotometer traces of the beginning of the 0–0 band (Fig. 2) show clearly that of the P-doublet the right-hand component (i.e. the one with the higher wave-number) is the most intense. The appearance of lines not overlapped on the trace gives no indication of asymmetry, so that we conclude that the higher wave-number components are the P_1 lines. This identification coincides with that one arbitrarily chosen by Sen.

No satellite branches were observed.

Rotational constants

The rotational constants B_v and D_v were determined graphically from plots of $\frac{1}{2}\{\Delta_2 F_1(K)+\Delta_2 F_2(K)\}$ against $K(K+1)$. The observed B_v and D_v values are given in Table 1. The B_v'' values follow the equation

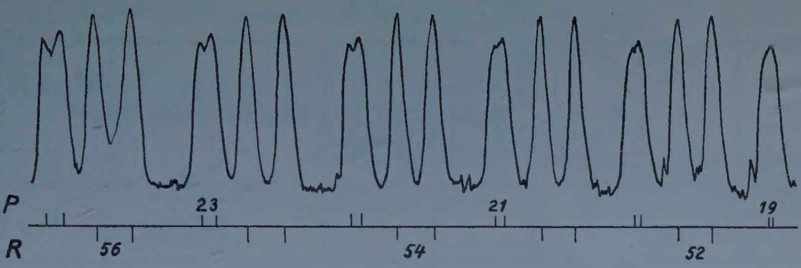

Fig. 2.

Table 1. Rotational constants in cm^{-1}.

v	B_v''	B_v'	$D_v'' \times 10^6$	$D_v' \times 10^6$
0	0.6384	0.6018	1.11	1.16
1	0.6328	0.5974	1.13	1.16
2	0.6268	0.5929	1.14	1.16
3	0.6210	0.5884	1.14	1.15
4	0.6153		1.17	
5	0.6095		1.24	

$$B_v'' = 0.6413_6 - 0.0058_0\ (v+\tfrac{1}{2});$$

the B_v' values $$B_v' = 0.6040_8 - 0.0044_7\ (v+\tfrac{1}{2});$$

the D_v'' values $$D_v'' = [1.08 + 0.02\ (v+\tfrac{1}{2})] \times 10^{-6}.$$

The variation of D_v' with v has not been detected. We find

$$D' \approx D_e' = 1.16 \times 10^{-6}\ \mathrm{cm}^{-1}.$$

The internuclear distances r_e' and r_e'' are

$$r_e' = 1.6668; \qquad r_e'' = 1.6176 \times 10^{-8}\ \mathrm{cm}.$$

The difference between the splitting constants γ' and γ'' were determined as the slope from plots of $\Delta\nu_{12}(\mathrm{P})$ and $\Delta\nu_{12}(\mathrm{R})$ against K. The values derived are:

$$\gamma_0' - \gamma_0'' = 0.0127 \qquad \gamma_1' - \gamma_2'' = 0.0157$$
$$\gamma_1' - \gamma_1'' = 0.0146 \qquad \gamma_0' - \gamma_2'' = 0.0162$$
$$\gamma_0' - \gamma_1'' = 0.0138 \qquad \gamma_1' - \gamma_3'' = 0.0184$$

For the 0–0 band, where the wave-numbers of the lines are most accurately known, γ_0' and γ_0'' have been determined from the combination differences. The result is

$$\gamma_0' = (21 \pm 5) \times 10^{-3}; \qquad \gamma_0'' = (10 \pm 5) \times 10^{-3}\ \mathrm{cm}^{-1}.$$

Vibrational constants

The origins of the bands were obtained graphically from plots of $\mathrm{R}(K-1) + \mathrm{P}(K)$ against K^2. Values are collected in Table 2. The vibrational constants, calculated from these values of ν_0, are as follows:

Table 2. Origins of AlO bands.

3									18516.1
2								18576.75	
1			20533.04	951.55	19581.49	937.36	18644.13		
			863.09		862.99				
0	20635.18	965.23	19669.95	951.45	18718.50				
v' / v''	0		1		2		3	4	5

$$\omega_e'' = 979.23 \text{ cm}^{-1}, \qquad \omega_e' = 870.05;$$

$$x''\omega_e'' = 6.97, \qquad x'\omega_e' = 3.52;$$

$$T_e = 20688.95.$$

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